Measurement of Ion Transport Properties, Ion Reaction Rates, and Trace Neutral Concentrations of Atmospheric Interest.

Final Report

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FINAL PROJECT REPORT
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PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Inst. of Technology - Engineering Exp. Station - 225 North Ave., N.W. Atlanta, GA 30332		ATM 8016881
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PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

The transport properties of several ions of atmospheric interest have been studied as a function of temperature in a high pressure drift tube mass spectrometer. As a result the ion mobilities of NH_4^+, Cl^- and Br^- in N_2 and NH_4^+ and Br^- in O_2 were measured at temperatures from 300-660°K.

A brief air sampling study was conducted using the drift tube mass spectrometer to study ions artifically produced in air and having lifetimes of less than one second. While this preliminary study gave some insight into the ion species one might find in the troposphere, its most important contribution was to inspire the development of an apparatus capable of directly sampling ions in the lower troposphere. This appratus can detect and mass identify ions in ambient levels (10^2-10^3 ions/cm^3) where they make up only about one part in 10^{17} of the total atmospheric gas. The newly constructed mass identified tropospheric ion sampling apparatus underwent several major improvements as well as a considerable amount of laboratory testing and performed well. By the end of this grant period this apparatus was ready to be used in preliminary field studies.

The use of this instrument for tropospheric ion sampling is expected to open the door for an increased understanding of the nature and number of ions present in the lower troposphere, and thus allow investigation of the ion chemistry and possibly aerosol formation mechanisms in this region of the atmosphere which is not possible until these ions are identified. The monitoring of ions in the troposphere also can provide an extremely sensitive detector (down to 1 part in 10^{15}) of certain trace neutral constituents having very low ionization potential or high electron or proton affinities.

The ion mobilities which have been measured during this grant are needed for ion-ion recombination rate calculations and to evaluate ion collection efficiencies in ion reaction rate measurements. They also provide an additional physical parameter by which ions may be identified.

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses	X				
b. Publication Citations		X			
c. Data on Scientific Collaborators					
d. Information on Inventions	X				
e. Technical Description of Project and Results		X			
f. Other *(specify)*					

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
Fred L. Eisele Earl W. McDaniel		6/3/83 June 12, 1983

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Final Report

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A great deal of progress in the area of tropospheric ion detection and identification has been made during this grant, in addition to the measurement of several temperature dependent ion mobilities. Much of the development of a mass identified tropospheric ion sampling apparatus (which is described in this report) was made either simultaneously or in alternating successive stages with the measurement of ion mobilities in order to conserve time and funds. Progress will therfore be listed in approximate chronological order in this report.

A. Mobility Measurements of Cl^- in N_2

The first measurements performed during the present grant period (which began on September 1980) were of the mobility of Cl^- in N_2 over the temperatute range 460-640 K. These measurements were published in the September 1, 1981 issue of the Journal of Chemical Physics.[1]

B. Initial Air Sampling Measurements

During the same time period the design and construction of the proposed air sampling system was underway. This system allowed the direct and rapid transport of air from well beyond the outside of the Baker Building (in which our laboratory is housed) into our High Pressure Drift Tube Mass Spectrometer (HPDTMS). The sampling system consisted of a 9-meter long, 10 cm diameter teflon coated aluminum tube, extending from our laboratory to 4 meters above and beyond the side of this building. A blower capable of pulling air through this sampling tube at 2000 cm/sec was installed at the laboratory end of the tube. Sampled air was extracted from this tube about 1 meter before it reached the blower. For the initial studies this air sample passed through a leak valve and into the HPDTMS where it mixed with the nitrogen drift gas. The drift tube was operated at several hundred degrees centigrade and at drift gas pressures slightly below one atmosphere. A high drift gas temperature and a drift tube gas mixture

containing only a small fraction of air were employed in an attempt to keep the observed spectrum simple by shifting the equilibrium for ions such as $A^{\mp}(H_2O)_n$ to lower values of n. Over a period of several weeks the fraction of the total drift gas made up of outside air was increased to unity and the drift gas temperature was gradually lowered to room temperature. The final sampling method in this sequence of measurements involved the use of a second blower to pull air out of the 9-meter sampling tube through a thin 5 micron ($\sim$10% transmitting) grid and then through the drift tube. The 5 micron grid had to be used to stop dust particles that could clog the 25 micron exit aperture of the drift tube. This method, as shown in Figure 1, allowed air sampled from well above the roof of our building to reach the drift tube in less than 1 second, with a minimum of contact with foreign surfaces.

Once the air sample enters the drift tube, a small fraction of it is ionized by high energy electrons from a radioactive Ni^{63} source. The ions formed then reacted in the drift gas (air) from 10-200 milliseconds, after which a small fraction of these ions from the central core of the ion swarm pass through a 25 micron exit aperture. They are then mass selected by a quadrupole mass spectrometer and detected by an electron multiplier. Problems of ion cluster formation and/or breakup in or near the exit aperture are discussed at the end of this section. By comparing the mobilities of $A^+.(N_2)_n$ for $n = 0$ and higher values, it was determined that most of these nitrogen clusters were formed at the exit aperture. It is expected that ions clustered with water, such as $A^+.(H_2O)_m$ where $m > 0$, exist in the drift tube but depending on the temperature, pressure and water content of the air these clusters generally have a value of m which increases as they pass through the exit aperture.

Our primary intent in this study was not to identify the size of ion clusters due to clustering reactions with common constituents of air, such as N_2 or H_2O. Rather, our aim was to try to identify the core ion and trace atmospheric constituents which might have formed a cluster

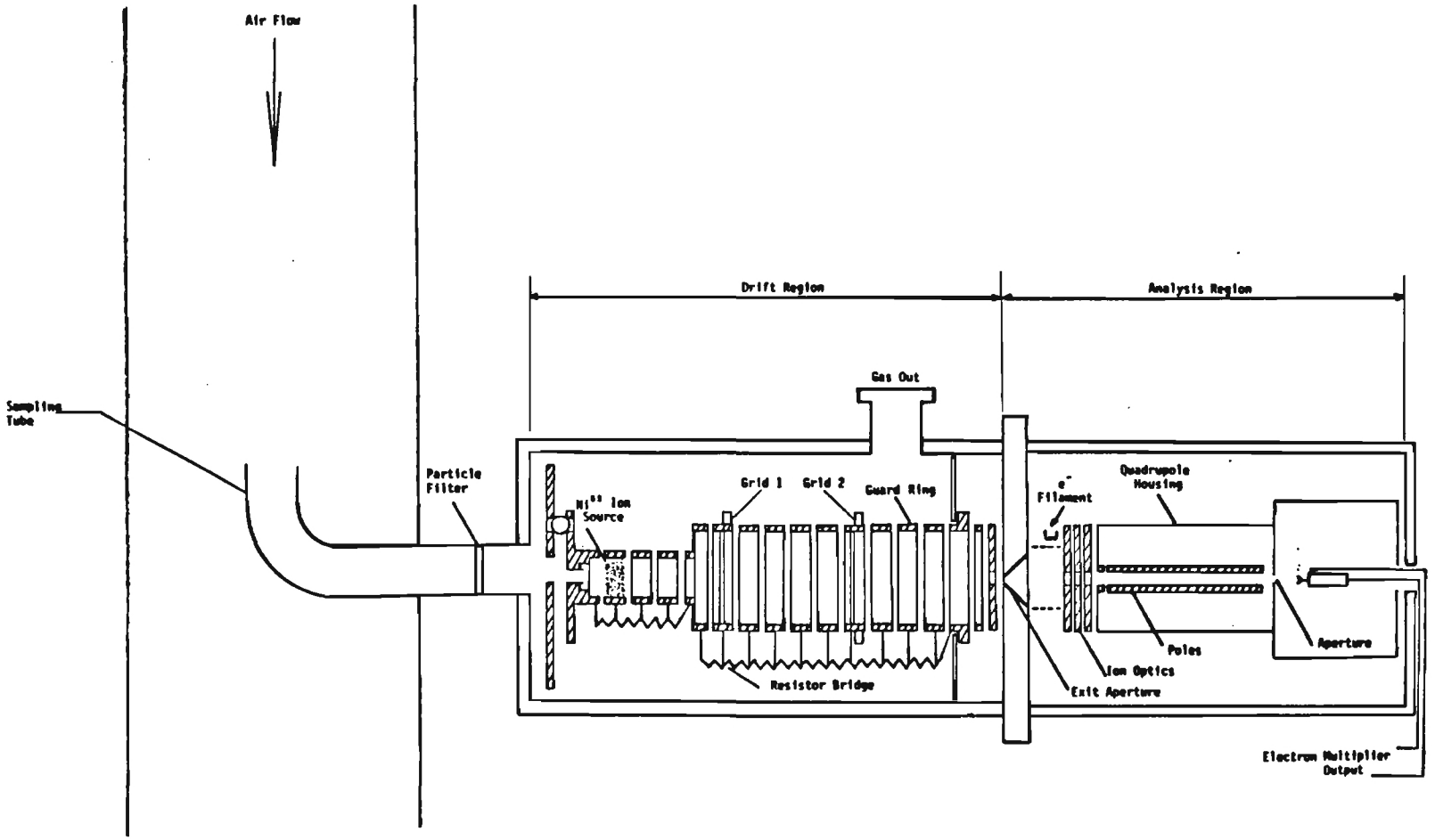

Figure 1. HPDTMS Air Sampling Apparatus.

with the core ion. In order to insure that the observed ions resulted from the ionization of, and ion-molecule reactions in the sampled air and not from contaminants in the sampling tube, filter grid or other components, clean, dry nitrogen was flowed down the 9-meter sampling tube. The blower was turned off and the top of the sampling tube was closed and N_2 admitted just a few centimeters below it. This procedure allowed the N_2 to fill the entire sampling tube and flow out through he blower. A small fraction of this N_2 went through the drift tube just as the sampled air did. The resulting spectra could then be compared to those obtained during direct air sampling. The results of the measurements are discussed later in this section.

Wind speed and direction, as well as outside temperature and humidity were recorded along with the mass spectra. Records of the wind direction, in particular, were necessary to ascertain whether any of the observed ions could have been caused by emissions from the building's vents or blowers. No correlation between wind direction and ion spectra was found. Since there are no other buildings or known sources of contamination in the near vicinity we have tentatively assumed that the air sampled was typical of this part of the the city of Atlanta.

Air sampling experiments were performed for about four months, over a variety of drift tube temperatures and pressures and under varying atmospheric conditions. The earliest experiments took place at elevated drift tube temperatures ($\tilde{\sim}$ 600 K), reduced pressures (400-700 torr) and with only a fraction of the drift gas being air. The remainder of the drift gas was high purity N_2. A typical positive ion spectrum corresponding to these parameters is shown in Figure 2. When the drift gas approached 100% air and the drift tube temperature was decreased, the spectra became more complicated, as shown in Figure 3. Finally, Figure 4 shows a spectrum taken at a pressure of 737 (atmospheric pressure in Atlanta) torr of air at $25^{o}C$.

Several expected changes are seen to occur as the temperature is decreased and the sampled air pressure increases. The size of ions clustered with water increases (i.e., they move up the mass spectrum 18

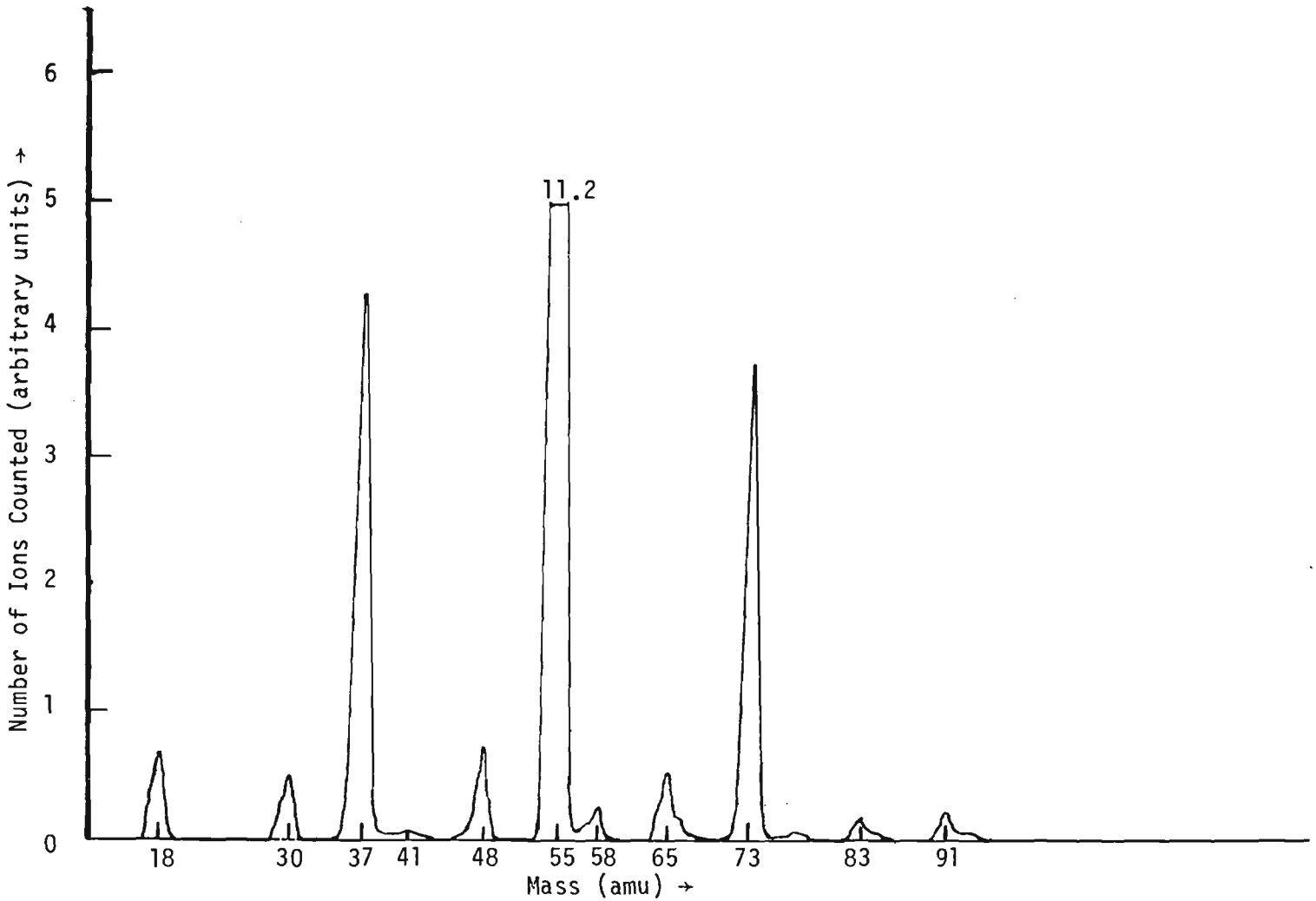

Figure 2. High Temperature Spectrum of Ions Produced in Sampled Air (The number on top of the 55 amu peak is the total height of that peak given in the unit shown on the left-hand axis.)

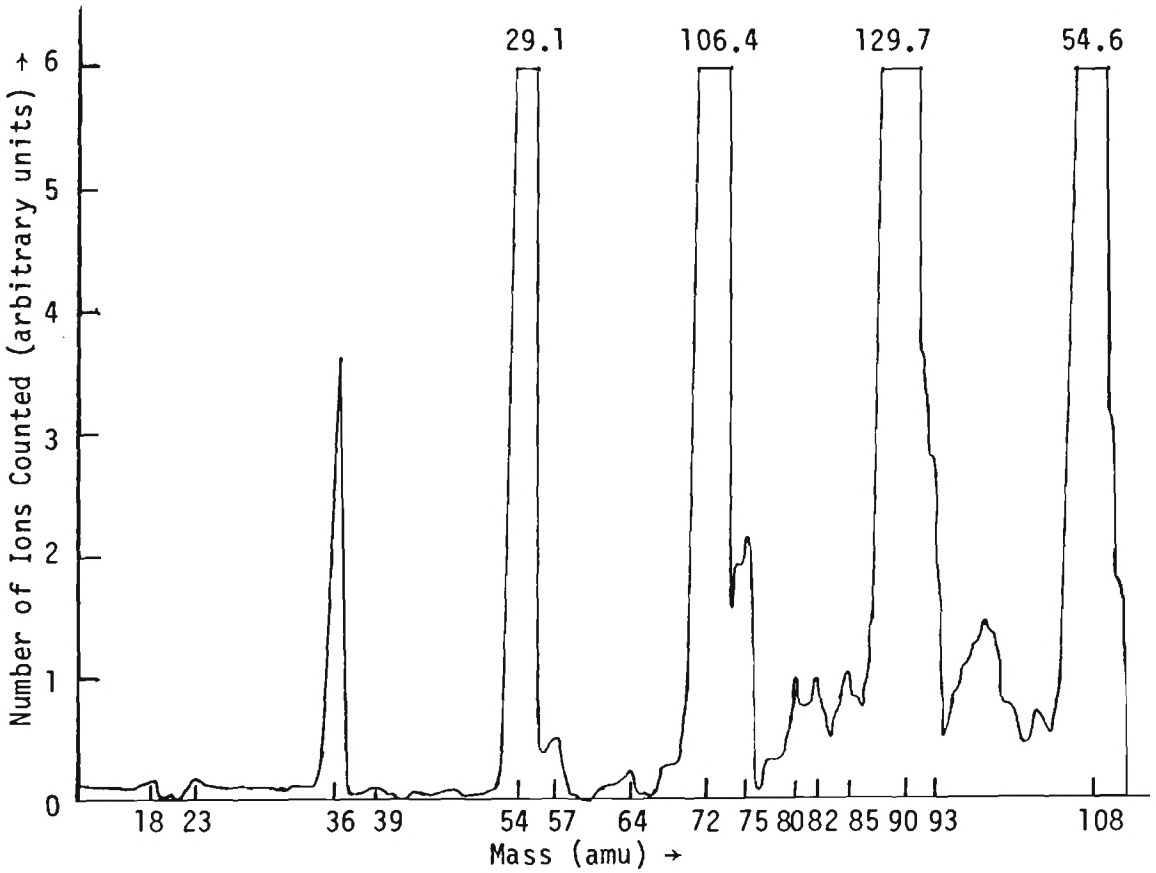

Figure 3. Intermediate Temperature Spectrum of Ions Produced in Sampled Air (The masses specifically labeled are just some of the more dominant and persistent ions observed during this study. The numbers above the flat-topped peaks are the total height of those peaks in the units shown on the left-hand axis.)

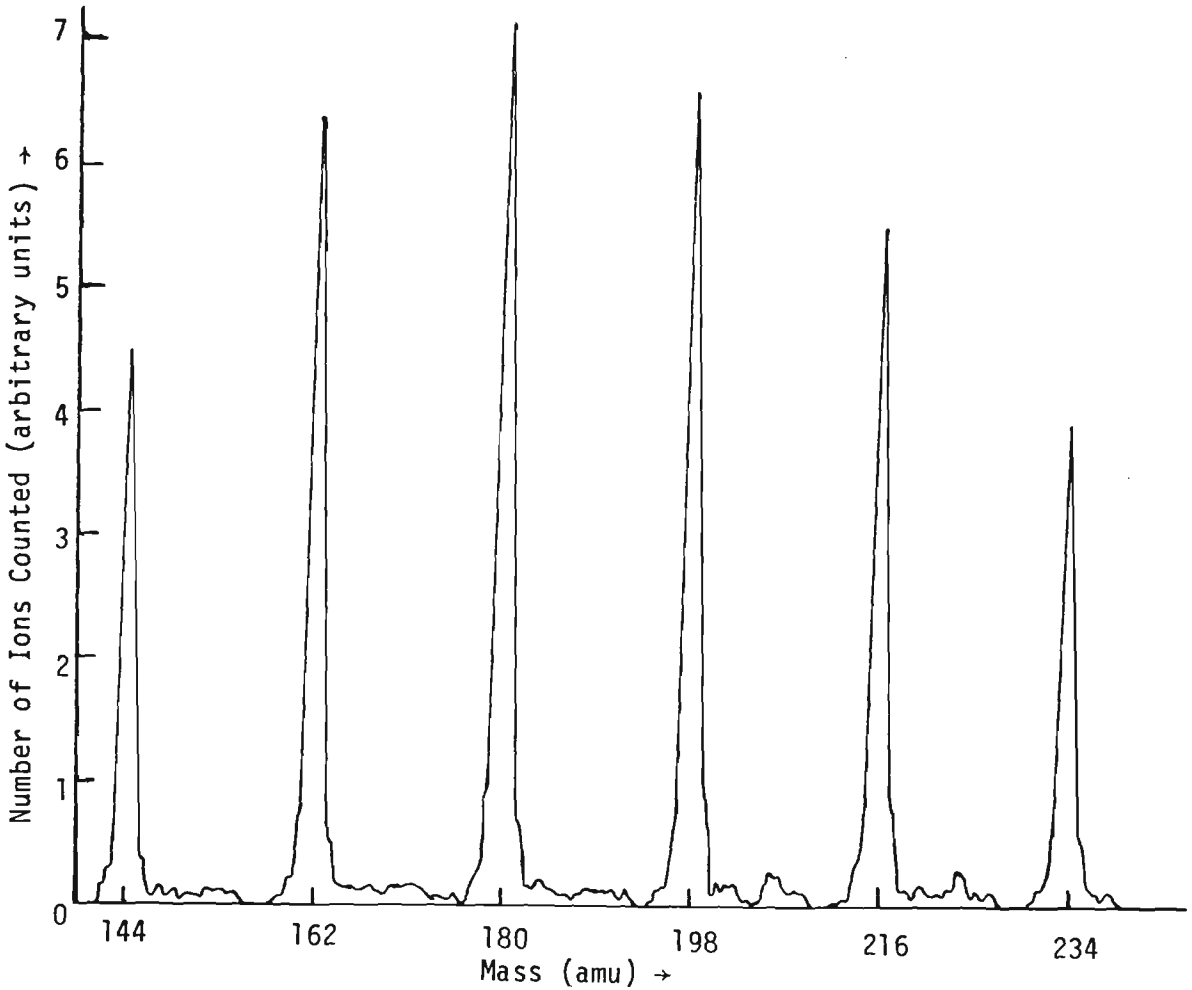

Figure 4. Ambient Temperature Spectrum of Ions Produced in Sampled Air.

mass units for each additional water molecule added) as the partial pressure of water increases and as the equilibrium for a clustering reaction shifts to high n values at lower temperatures. Ions clustered with N_2 follow the N_2 partial pressure and temperature in a similar manner (an increase of 28 atomic mass units per N_2 molecule is seen in Figures 2,3.) The partial pressure of other trace atmospheric constituents, some having very high proton or electron affinities, also increases as the pressure of the air sampled increases. Thus new core ions are observed as these trace (high proton and electron affinities) parent molecules become sufficiently abundant to undergo charge or proton exchanging reactions with the previous charge carrier. (The fact that clustering reactions and charge or proton-exchange reactions are considered separately above is in no way meant to imply that clustering has no effect on the choice of the core ion, or that the rate of clustering is independent of the identity of the ion core. Charge or proton exchange and clustering reactions are considered separately only to simplify this discussion.)

Ion spectra such as those shown in Figure 2-4 can give considerable insight into the ion chemistry and neutral concentration in the troposphere. It must be remembered, however, that these spectra do not directly describe ions present in the troposhere or even in the drift tube. The apparent N_2 clusters seen in Figure 3 have been observed several times in the drift tube under more controlled conditions during the mobility measurements of specific ions in one atmosphere of high purity N_2. During these experiments the arrival times of the N_2 clusters of the ions of interest were observed to be identical (to within our measurement capacity) to the arrival time of the core ion. It was thus concluded that these N_2 clusters were formed at the exit aperture and were not present in the drift gas. Though similar measurements have not yet been directly performed in air, due to large and varying water concentrations, it appears doubtful that many core ions undergo significant stable N_2 clustering at or above 300 K in the

drift tube. Water clusters do exist in the drift gas and can be observed even at extremely low water concentrations, where virtually no ion-water molecule collisions can occur in the exit aperture, due to such low water concentration and a limited number of possible collisions. While water clusters do exist in the drift tube, under air sampling conditions, the observed spectrum is expectedto be shifted somewhat due to reactions occurring in and around the exit aperture. The electric field just beyond the exit aperture is quite low as discussed later in this section. Thus the core ion is in general expected to be preserved in its passage through the exit aperture, except that it may be found distributed among several additional N_2 and H_2O cluster peaks in the mass spectra. In addition, some mass discrimination effects are undoubtedly present, due to the exit aperture geometry and the quadrupole mass spectrometer itself, which was not calibrated for this initial atmospheric sampling experiment. It must be remembered that the observed spectra are typical of ions drifting in air from 10-200 milliseconds and are not expected to be the same as the terminal ion species present in the lower troposphere having lifetimes of several hundred seconds.[2]

Several important observations have been made in this preliminary study. NH_4^+ was seen to be a very prevalent core ion in the positive spectrum. This ion was identified both by mass and by a back-to-back mobility measurement. (This back-to-back measurement was accomplished at elevated temperatures, where there was little clustering, by measuring the mobility of the mass 18 ion in the air being sampled. Then, immediately after this measurement, a very small amount of NH_3 was added to the drift gas made up of similar air being sampled only minutes later, and the mobilities were measured to be the same.)

It also appeared from the ion spectrum taken over an extended period of time that the NH_3 concentration rose during and after a rain storm. $H^+.(H_2O)_n(N_2)_m$ was also observed in the positive ion spectrum but only as a minor component (at ambient temperatures). This ion family was identified only by its masses, but has been previously observed in air and other gases by ourselves and many other investigators. Several other apparent positive ion families have been observed but their identities remain a matter of speculation. Due to

their low intensities, it would not even have been obvious that some of them were families except that their growth to higher order clusters was observed as the drift tube temperature was lowered. Three such sets of families were observed which had the appropriate masses to be $NO^+(H_2O)_n(N_2)_m$, $K^+(H_2O)_n(N_2)_m$, and $Na^+(H_2O)_n(N_2)_m$.

It would not be at all surprising for $NO^+(H_2O)_n(N_2)_m$ to be present in the drift gas. NO^+ is often observed in clean O_2, N_2 gas mixtures. It has a low ionization potential, and the lowest mass observed in one of the ion families was 30, which could correspond to the NO^+ core ion.

If NO^+ was the core ion observed, it may have been formed either in a charge-exchanging process from a trace atmospheric constituent or from N_2 and O_2 in the initial ionization process. The lightest ions observed in the remaining families (also observed at 500-600 K drift gas temperature) were 23 and 39 which suggests that Na^+ and K^+ may be the core ions. Unfortunately, signal level was too low to permit a search for an isotope at 41. A small peak was on occasion observed at 41, but it was too large to be an isotope of potassium. Rather, it appeared to be related to the Na^+ family.

In the negative spectrum at elevated temperatures Cl^- and Br^- families in general dominated the spectrum. These ions could be identified both by their mass and their isotope ratio; hence their identification was quite certain. At 300 K some Cl^- remained in the spectrum, but other ion families became dominant. Unfortunately, it is difficult to identify a family such as $A^-(H_2O)_n(N_2)_m$ where n = 2-10 and m= 0-3 are common and little helpful information can be derived from measurements performed as a function of temperature. This situation is made worse by the apparent variation of the core ion from day to day. However it is possible to suggest that the core ions NO_2^-, NO_3^-, CO_4^- and/or O_2^- could have been responsible for the observed ion cluster series. Their families overlap for the range of n and m values observed and no clear identification was made.

Background measurements were made under conditions similar to those of air sampling, except that the 9-meter long sampling tube was filled with N_2 flowing in the same direction as the sampled air. These measurements suggest that the parent molecules of water and ammonia were clearly coming from the sampled air. The parent of the NO^+ family is not clear because of its possible origin from the ionization process as mentioned above. Low mass members of the Na^+ and K^+ families were observed in the background. Because of the low signal and their shift to many additional, more massive clusters in wet air, we cannot be sure of their origin. Cl^- and Br^- ions were also present in the background, but their large peak height changes compared to that of other ions suggest an atmospheric source of chlorine and bromine. The other major negative ion families observed also appear to have their origin from the atmosphere.

Our inability to remove certain trace parent molecules from the sampling path does not mean that they did not originate from the sampled air. One substantial problem with this sampling method is that the air sample must pass through a filter or grid which removed particles larger than about 5 microns in order to avoid clogging up the sampling aperture. This grid fairly quickly gathered a great many particles and probably trapped some gases which then remained in the sampling path both during sampling and background runs.

Some of the difficulties encountered in these experiments can be minimized if additional improvements are made to the preliminary sampling apparatus. There are, however, several inherent problems associated with this or any similar sampling system which involves an ionization source in close proximity (both spatially and temporally) to the high vacuum sampling aperture. There are also several additional problems associated with allowing the sampled air to pass through the exit aperture. Many of these problems can be circumvented and some new capabilities are available using a direct ion sampling technique developed and tested in this laboratory. The use of this technique and the associated apparatus are a part of this report.

C. Mobility Measurements of NH_4^+ and Br^- in N_2

At the end of these initial sampling experiments ion mobility measurements were resumed. Because of the observations of NH_4^+, Cl^- and Br^- in air, the mobilities of NH_4^+ and Br^- were measured in N_2. A detailed discussion of this work describing the measurement of mobility values over a wide range of temperatures has been submitted to the Journal of Chemical Physics. A preprint of this article is included in this report as Appendix A. The mobility of Cl^- in both N_2 and O_2 have already been measured.[1,3]

D. The Possibility of Direct Tropospheric Ion Sampling

Simultaneously with the measurements of NH_4^+ and Br^- in N_2, the feasibility of a direct atmospheric ion sampling instrument was investigated. An electrode configuration was designed and constructed which, it was believed, would make possible the concentration and extraction (at an elevated potential) of ions from a flowing gas.

The geometry of these electrodes is shown in Figure 5 and is labeled flow opposed drift tube (FODT). This device consists of a grid followed by 11 circular guard rings which maintain an approximately uniform axial field in this region. The next four guard rings are then segmented such that a transverse field component can be superimposed on the axial field. The component of the electrical field parallel to the axis is also increased by a factor of 2 or 3 by the lower segments of this section and the final guard ring. Another set of circular guard rings extend out to one side of this device and are used to apply an electric field which will assist in extracting the ions from the gas flow. Figure 6 shows a sketch of the approximate direction and intensity of the electric field, the gas velocity and the ion *and* neutral gas trajectories. The use of a uniform electric field which terminates very abruptly at a grid accomplishes several goals simultaneously. The ions of interest have a drift velocity in this field which is less than the neutral gas velocity. Thus, the gas velocity can push the ions against the electric field, so that they end up at a potential well above ground. Since the average ion transport

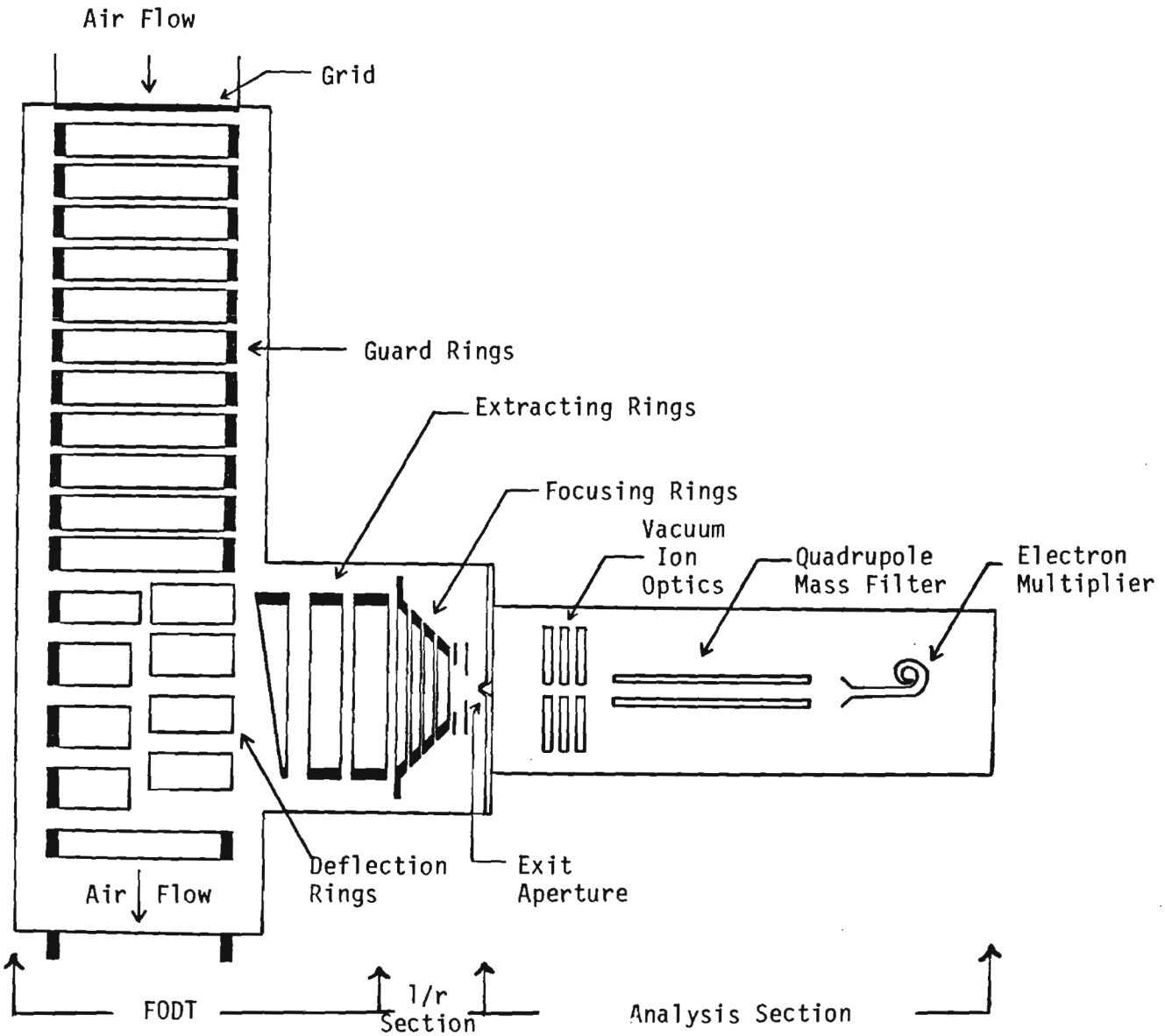

Figure 5. Direct Ion Sampling Apparatus.

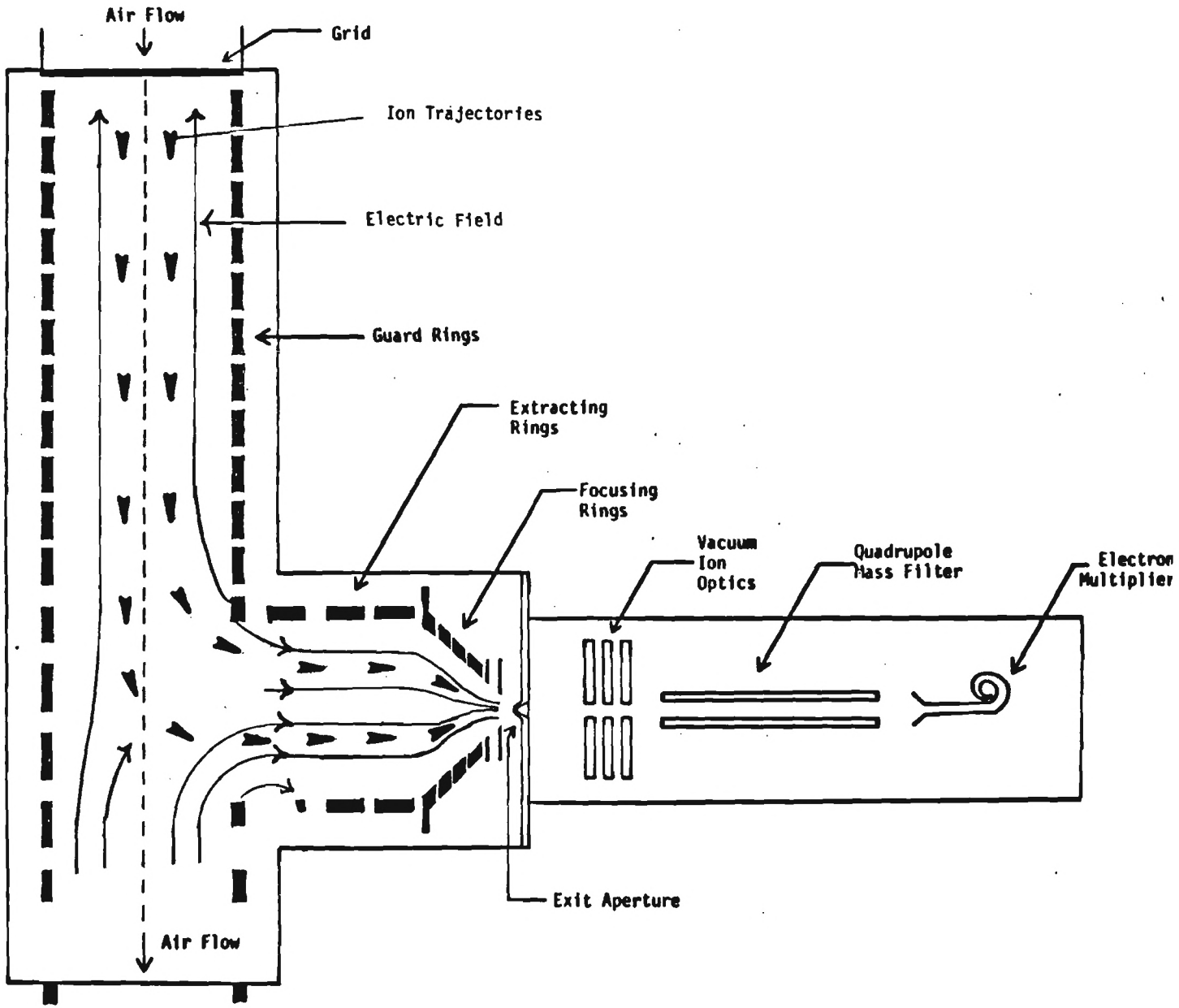

Figure 6. Approximate Shape of the Electric Field Lines in the Plane which Contains Both FODT Axes.

velocity decreases in this region, while the total number of ions passing through the region remains approximately constant, the ion number density must rise. The abruptly terminated uniform field is used in order to minimize the transverse field components which could push ions to the walls. In addition, this field makes modeling the ion trajectories somewhat easier in this already complicated turbulent gas flow. (While working with this flowing gas containing ions with a forward motion that were opposed by a uniform electric field, several additional applications of this technique become apparent. For example, a FODT could be used to continuously (in time) transmit or select a specific range of mobilities in order to select specific (charged) aerosols. Also under known and well controlled gas flow conditions, it could be used to greatly increase ion concentrations.)

In the segmented ring section of this device the axial field increased to a value sufficiently high to stop ions with a reduced mobility of greater than about 1.5 cm^2/V-sec from passing down the tube. This field should further increase the ion concentration. In this same region the relatively weak transverse field accelerates the ions out of the flowing gas and along the direction of the axis of the extraction rings. The ions at this point are still at a potential of several thousand volts above ground.

The inside diameter of all of the guard rings is 10 cm so as to match the sampling tube diameter. The outer tube which encloses these electrodes is about 14 cm I.D. and is reduced to 10 cm at both ends, again to match the air sampling tube.

This device was first tested in February 1981 and soon proved to be quite successful. Plans for the construction of the next stage of this apparatus were then begun. This section consisted of a series of six circular guard rings mounted to form a conical segment making a 45^o angle with its axis as shown in Figure 5 and labeled focusing rings. Voltages were then applied to these electrodes in order to produce an electric field with a potential gradient $1/r$ (where r is the distance measured from the origin located on axis and about 0.15 cm behind the exit

aperture) over most of the enclosed volume. For values of r equal to the length of this section, the field gradually undergoes a transition from the fields of the 1/r potential region to the fields produced by the ion extraction guard rings. Near the origin the electric field lines again become parallel due to the boundary conditions imposed by the exit aperture geometry. The results of a computer computation which modeled the fields in this region are shown in Figure 7. The purpose of this field is to take the ions passing through the 10 cm diameter extraction rings and focus them down to about a 1-2 cm diameter circle. (At these high pressures the average ion trajectory will simply be along an electric field line.) Additional focusing was restricted by the ratio of the initial field intensity to the desired (zero field conditions) final field intensity, rather than by diffusion. This focusing resulted in a greatly increased ion flux density and ion drift velocity along the axis, but not in an increased ion density. This increased ion drift velocity (which, because of the 1/r potential, could be obtained without a decrease in ion density) was then used to push the ions out of the air in which they were found and into high purity N_2 and finally on into the exit aperture. The N_2 filled the area immediately around the exit aperture and left that area through the opening in the guard ring closest to the exit aperture at a velocity of several hundred cm/sec in the opposite direction of the ion drift velocity. The purpose of the N_2 was two-fold. First it prevented dust particles from clogging the exit aperture without the use of any type of filter. Secondly, it allowed the sampled ions to undergo addition and dissociation reactions in the clean N_2, which contained much less water than that found in air. Thus n, the number of water clusters, is shifted to a much lower number, making the observed ion spectrum much easier to interpret. Since the N_2 partial pressure is about 20% higher than that in air, some additional N_2 clustering occurred, however far fewer water clusters were observed. (Gases other than N_2, such as Ar, can also be used for this purpose.) Because the ion spends only a few msec in this environment, additions or losses from the ion clusters in

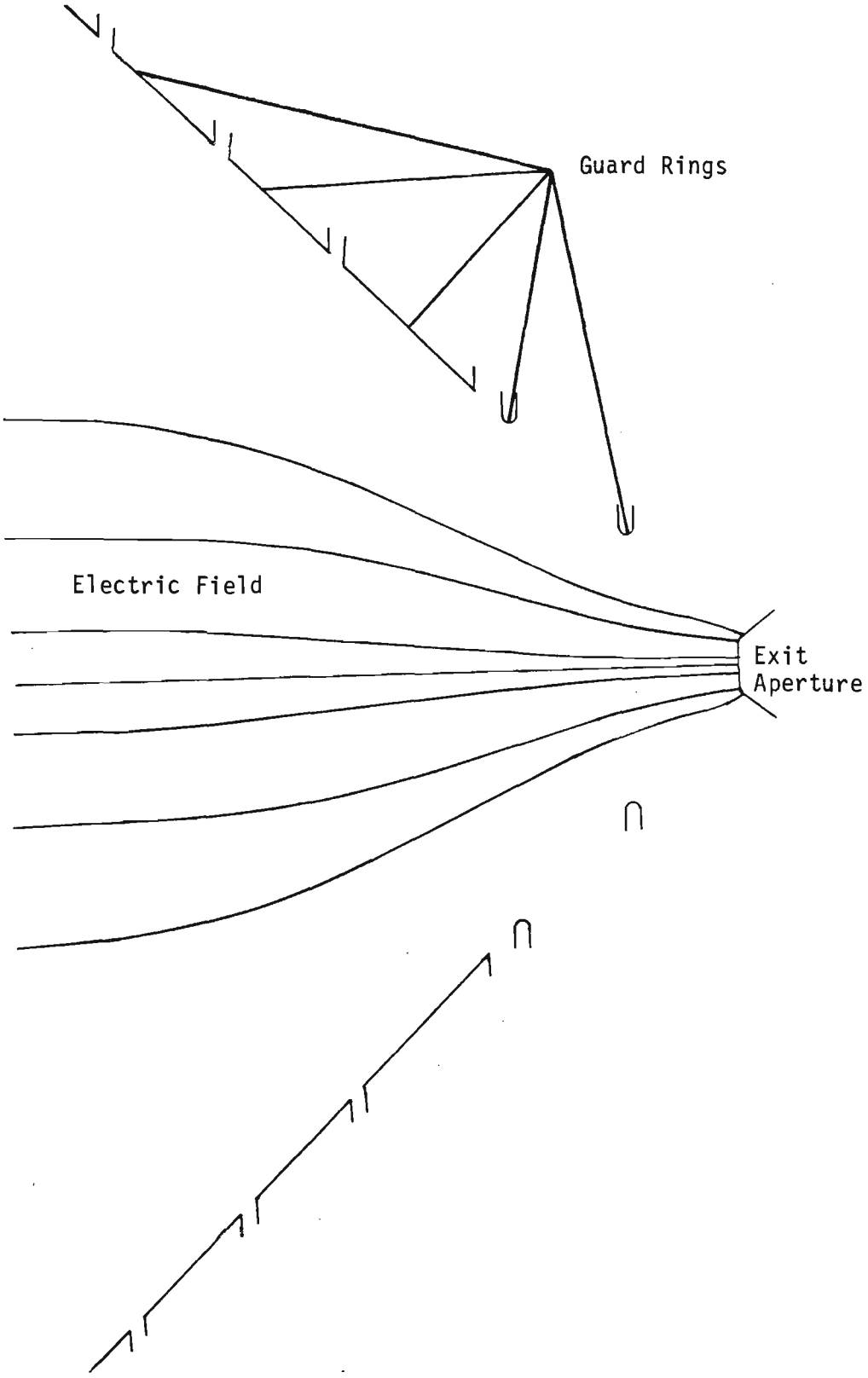

Figure 7. Computer Model of the Electric Field in the 1/r Region.

this region are expected to be caused by the addition or loss of some molecules present in the ppm concentration range or higher that will readily cluster with the sampled ion. Unwanted molecules at this high concentration in the N_2 which readily form clusters or undergo charge-exchange can easily be identified. The present apparatus was not expected to detect terminal ions that had parent molecules in concentrations as high as the ppm range. Of course, a modified system using filtered air around the exit aperture would have this capability.

The FODT and the conical 1/r potential sections were tested together in the late spring of 1981 (at the completion of the NH_4^+ and Br^- mobility measurements in N_2). There appeared to be a small number of ions being detected from beyond the end of the 9-meter sampling tube outside the building, but there was not a sufficient number to mass analyze. The origin of ions from somewhere other than beyond the sampling tube can be determined by the use of several shutter grids along the tube or by the variation of a number of other parameters such as gas flow rate and electric field intensity. At the end of nearly two months of testing, we decided to go back and try to answer some of the many questions which arose during these tests. This break also allowed the continuation of the proposed mobility measurements.

E. Mobility Measurements of NH_4^+ and Br^- in O_2

Observation of NH_4^+ and Br^- in our air sampling experiments and measurements by others of neutral NH_3 and Br-containing compounds in the troposphere suggested the importance of these ions. It was felt that since we had already measured their mobilities in N_2, a measurement in O_2 would allow a very accurate calculation of their mobility in air. This measurement was thought to be not only of importance for atmospheric modeling, but it could also be used as a means of identification of these ions in air at elevated temperatures. Thus the mobilities of NH_4^+ and Br^- in O_2 were measured over an extended temperature range. The results of these measurements have also been submitted for publication. A preprint of this material is included in Appendix A.

F. Computer Modeling of Ion Sampling Apparatus

While the mobility measurements were ongoing, the electric field in and around the 1/r potential section was modeled. In particular, our interest was in the shape of the field on or near the axis at either end of the 1/r potential section. The computer modeling was done using fixed nodes to represent the boundary conditions imposed by the metal guard rings and floating nodes for the space in between. These nodes formed a two-dimensional array of points in a plane, which included the axis of the 1/r potential section. Their density was varied, depending on the resolution desired. All of these nodes were then interconnected by conductors whose value was adjusted to simulate the effects of the three-dimensional geometry. The results of this modeling for the 1/r potential are shown in Figure 7. This particular model used about 300 nodes and 500 conductors. It should be noted that the electric fields in both the FODT and the 1/r potential regions were maintained at a sufficiently low value (zero-field region) so as not to disturb the energetics of the ion-chemistry.

G. Initial Direct Ion Sampling Measurements

By fall 1981, most of the computer modeling was completed, and the NH_4^+ and Br^- in O_2 mobility measurements were finished. Various alterations and improvements were then made to the ion sampling system. The drift tube was then removed from the mass spectrometer and again replaced by the ion sampling system. The various guard ring potentials on the FODT and 1/r potential sections were optimized for the mass range of 100-300 amu and a new electron multiplier was installed. Initial tests with these modifications demonstrated a 50-fold improvement in signal to noise. These measurements were made with the mass spectrometer operating in the integral mode, as was done for the earlier measurements. The integral mode is an extremely low resolution mode in which ion masses in or near a preset mass range (often 100-200 amu) are transmitted. This mode of operation results in several times the signal obtained when looking at a single ion mass which strongly dominates the spectrum. In order to insure that the observed ions originated from

somewhere beyond the sampling apparatus, a grid was placed at the entrance to the sampling tube where the tube diameter increases to about 25 cm diameter. Here the air velocity is significantly less than in the rest of the sampling tube; thus, the ions can be stopped with a much lower field strength. (A large horn shaped entrance to the sampling tube is used to minimize turbulence at the entrance by providing a more gradual but extended flow transition region.) When the grid was biased so that it would stop most of the ions from entering the sampling tube, a background measurement was made (10-20 counts per 100 seconds.) A small number, but only at mass 28, were seen to originate from the region of the exit apertures. None were observed from electrical breakdwon around the guard rings, unless they got very dirty. Most of the background probably consists of ions that are not stopped by the grid. (Due to the rapid build-up of elongated dust or hair-like particles, this grid, as is the case for any other grids placed in the main gas flow region, must be maintained at a relatively weak field if it is to be used for an extended length of time.) The grid potential was then reduced to zero so that the entrance of the sampling tube was all at ground potential. The ion flux was then sampled and found to be several times the background (30-100 counts per 100 sec depending on the day and atmospheric conditions). An attempt to measure the identity of the ions observed was then begun. When the quadrupole mass spectrometer was switched from the integral mode of operation to looking for specific single amu ion species, it was realized that the signal to noise ratio, even over extended time periods, might be too low. If at least one of the ions to be measured did not make up at least 10-20% of the total ion spectrum between 100-200 amu it would not be possible to resolve it from the noise. It appears that we got lucky. The spectrum was scanned one mass unit at a time, spending about 10 minutes per mass unit. A few small peaks were observed. Once observed, they were repeatedly compared to other masses where no peak was observed. These measurements were obviously quite slow, and the statistics were poor. There did appear, however, to be a fairly consistent peak at 151

amu which lasted for several days, then disappeared and reappeared after an interval of a few days. This peak may have been associated with drier weather. Another peak which was not observed initially, but appeared later for a couple of days was at 173 amu. Other possible peaks were at 159 and 188 amu. Attempts were made to see if the grid at the entrance to the sampling tube could be used to cut off a particular ion peak to show that it specifically originated from the atmosphere. The result was positive, but statistically unmeaningful. It was very apparent that more signal would be very desirable.

H. Improvement to the Direct Ion Sampling Apparatus

Since the ion flux had already been maximized in front of the exit aperture, in order to increase signal levels further one obvious modification was to increase the size of the exit aperture. A larger aperture would, however, require an increased amount of pumping. Thus a completely new pumping system was designed and its construction and assembly were completed in March 1982. This system is shown in Figure 8 and is pumped by two 10 inch oil diffusion pumps which were available in our laboratory. These are used in a newly constructed two-stage differentially pumped system. The first stage operates at about 10^{-3} torr and will pump about 30 times the gas load of the older vacuum system. The second stage will pump the quadrupole directly and reduce the pressure to the low 10^{-5} torr range in this region.

A new 4 component ion optics system was also built for this system and was designed to minimize ion cluster breakup. Sampled ions and neutral molecules now pass through a 140 micron diameter 25 micron long exit aperture and enter the vacuum region in a manner very closely approximating a free jet expansion. The expansion occurs in the presence of a weak electric field produced by the 4 component vacuum ion optics assembly. The amount of ion cluster breakup caused by the weak field appears to be quite small, as shown by the preliminary spectra taken under widely varying electric field conditions. This first set of vacuum ion optics focuses the ions through a 1 cm diameter skimmer which separates the 1×10^{-3} torr pressure region from the 3×10^{-5} torr

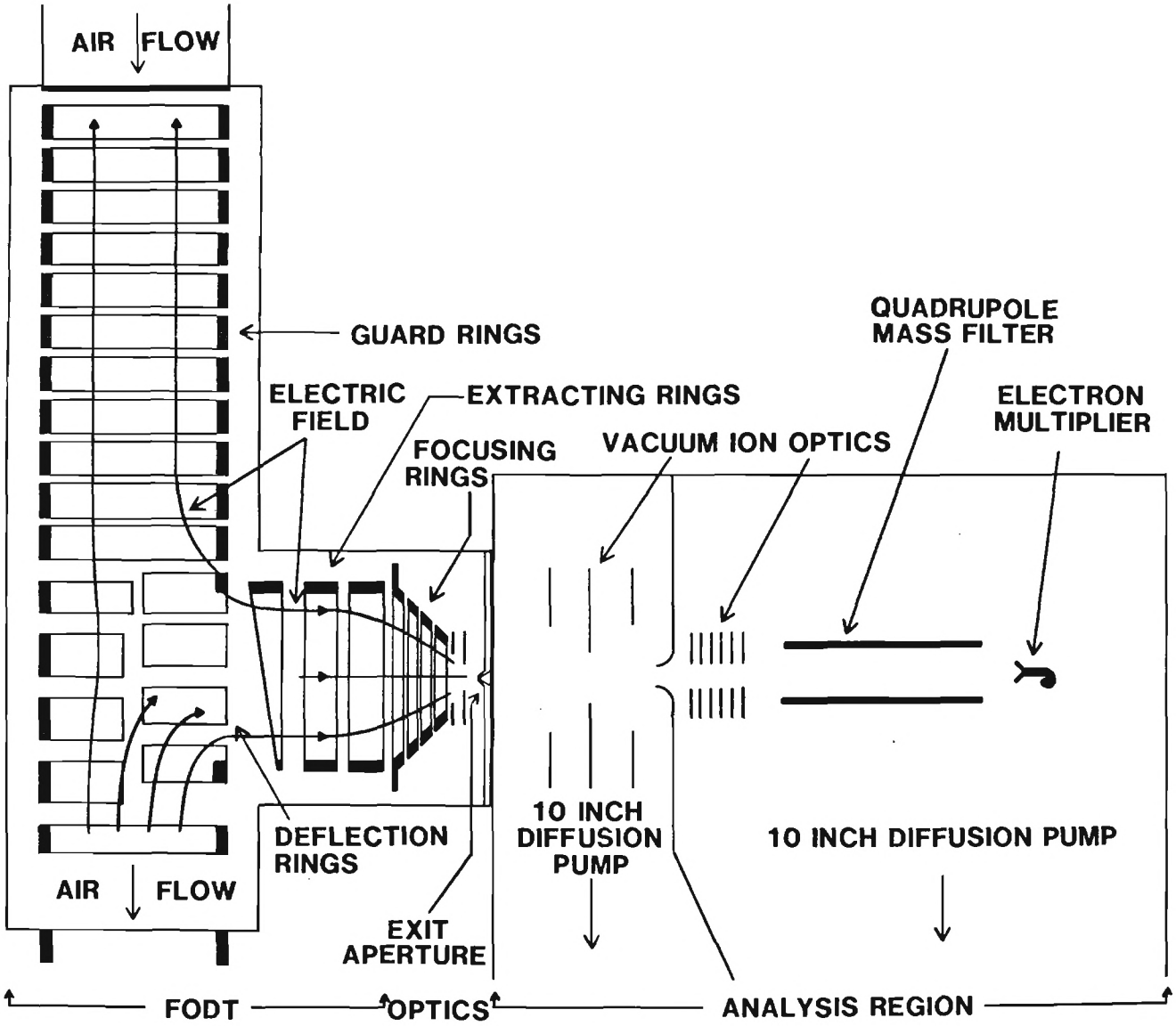

Figure 8: Mass Identified Tropospheric Ion Sampling Apparatus

region. In the high vacuum region the ions pass through yet another set of ion optics into a high resolution quadrupole mass spectrometer (Extranuclear spectrEL) and are detected by an electron-multiplier as before.

This new pumping system increased the number of detectable ions by about a factor of 20-30, thus making possible the detection of statistically meaningful ion mass peaks.

The background count rate for this device is about 0.02 counts/s; a single mass analyzed peak (1 amu resolution in the 200-300 amu range) will typically yield 0.05 counts/s; with a mass resolution of about 2-3 amu a detection rate of 0.1 counts/s can be obtained and with a near zero mass resolution, a count rate of 4 counts/s is measured. These values are for sampled air containing about 50 ions/cm^3 in the FODT region. The total ion concentration measurements were made by collecting the ions with mobilities >1 cm^2/v-s with a coaxial cylindrical condenser apparatus just after they passed through the FODT with its guard rings all held at ground potential. The time required to obtain a mass spectrum over a wide range of masses is obviously quite substantial, but an individual mass peak can be detected in 5 to 10 minutes.

With the increased signal levels now available, various measurements similar to those previously performed at lower signal levels have been made to help establish that the observed specific ion masses originate somewhere beyond the sampling apparatus. A double shutter grid assembly is periodically placed at the entrance to the sampling tube and/or just above the FODT region of the sampling apparatus. When the grid is "closed" (i.e., the electrical potential difference between the grids is made sufficiently high so as to stop nearly all the light ions of the polarity being measured from passing through the shutter grids) the ion counting rate again becomes close or equal to the background counting rate. The background rate is measured with the vacuum ion optics at a polarity opposite that normally used. Thus it appears that essentially all of the observed charge orginates

somewhere outside of the sampling apparatus itself. It does not, however, show that the observed ions are the same as those entering the sampling tube (i.e., that no chemical reactions such as ion-neutral reactions have taken place.) While we have no completely independent method of insuring that the apparatus or gases emanating from it are not involved in chemical reactions with the sampled ions, artificially produced ions themselves can be used to assist in detecting such reactions if they exist. A tesla coil was used to produce ions at the entrances to the sampling apparatus. The observed mass spectrum would not necessarily be expected to be the same as that of ambient sampled air ions (due to the much shorter lifetimes of the ions produced by the Tesla coil; i.e., less than 1 second compared to 10^2-10^3 sec.) unless the two spectra were both dominated by reactions with the sampling tube wall or gases emanating from it. In fact, the spectra appear quite different from each other. The directly sampled tropospheric ion spectrum is also observed to vary from day to day and within the period of one day under similar temperature conditions. This would probably not be the case if the ion chemistry were controlled by the sampling apparatus itself.

While the previously described experiments are not conclusive proof as to the origin or non-reactivity of the sampled ions they do lend reasonable support to this argument. Ongoing tests of this apparatus include moving the apparatus outside of the city of Atlanta, shortening the sampling tube length and observing ion spectra produced by different ionization sources.

The preliminary studies made with this apparatus have repeatedly (on many clear sunny days) shown positive ion mass peaks at 239, 240, 241 amu (with a resoluiton of about 1 amu). On overcast days these peaks appear to be less common. From time to time other masses appeared to be present, but the data are not sufficiently reproducible in these cases to be reported at present.

An important but initially surprising discovery made during the development of this apparatus is that despite the increase in ion flux at and around the exit aperture resulting from the use of the high pressure ion optics, no significant increase in the number of ions passing through the exit aperture could be detected. A wide variety of converging and uniform electric fields were tried with basically no change in the ion counting rate. Computer modeling was also used to determine the electric field intensity throughout the focusing optics and then at higher resolution in and around the exit aperture. The electric fields in front of and within the exit aperture combined with the gas flow through just the exit aperture still did not explain the absence of an enhanced counting rate. It is believed that the interaction of the gas flow and the electric field immediately in front of the exit aperture is the cause of the ion current remaining approximately constant, independent of the type of converging electrostatic focusing field used.

The direction of the electric field immediately in front of the exit aperture is to a large degree controlled by the plate containing the exit aperture. This plate is a flat nickel sheet about 20 times the exit port diameter. Since there are no other materials in the near vicinity of the exit aperture, the electric field is normal to the aperture plate and quite uniform near the exit port. This geometry is typical of many high pressure ion sampling apparatuses. Under weak electric field conditions, ions drift slowly towards the exit aperture plate in the direction of the electric field until they are diverted by the neutral gas flow leaving through the exit aperture. In order for the ions to be diverted sufficiently to pass through the exit aperture, the neutral gas velocity must in general be at least comparable to the ion drift velocity. For weak electric fields (i.e., where the ion drift velocity is much lower than the maximum exit gas velocity), the ions which pass through the exit aperture can originate from a drifting column of ions with a diameter much larger than the exit aperture. For much stronger electric fields, the diameter of the drifting column of ions from which ions will pass through the exit aperture (those ions for which the gas velocity approaches the ion drift velocity) becomes much smaller.

The decrease in the effective ion collection area is caused by the increased drift velocity parallel to the axis (in the stronger field) which carries many of the ions to the conductive surface around the exit port before they can be pulled through the aperture by the gas flow. It is expected that the decrease in ion collection area is approximately inversely proportional to the electric field strength, and thus cancels the effect of increased ion flux when a flux increase is accompanied by a similar increase in the electric field. This is not expected to be true if the ion drift velocity is greater than the neutral gas velocity at all points. The effects of diffusion are expected to be quite small at the high pressures (1 atmosphere), large concentration areas (4-100 cm^2), and short transit times (5-20 ms) that are used.

While the optics shown in Figure 7, may not in general be used to increase the ion concentration they can be used to increase the ion flux and to increase ion drift velocities while maintaining ion densities at a constant level.

Conclusions and Applications

The chemistry and wind patterns in our urban sampling environment are sufficiently complex that we do not at present wish to give any interpretation to the observed results except to conclude that the ion sampling apparatus is capable of sampling and mass identifying ions at ambient levels.

Field measurements in a less polluted environment are planned in the near future and it is expected that these will assist us in further evaluating our urban sampling results.

The use of this instrument for tropospheric ion sampling is expected to open the door for an increased understanding of the nature and number of ions present in the lower troposphere, and thus allow investigation of the ion chemistry and possibly aerosol formation mechanisms in this region of the atmosphere which is not possible until these ions are identified. The monitoring of ions in the troposphere also can provide an extremely sensitive detector (down to 1 part in 10^{15}) of certain trace neutral constituents having very low ionization potential or high electron or proton affinities. In addition, this device and the associated techniques such as the flow opposed drift tube can be used for a variety of sensitive ion or charged aerosol monitoring, separation, or control applications.

The ion mobilities which have been measured during this grant are needed for ion-ion recombination rate calculations and to evaluate ion collection efficiencies in ion reaction rate measurements. They also provide an additional physical parameter by which ions may be identified.

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APPENDIX A

Paper Submitted to the Journal of Chemical Physics

TEMPERATURE DEPENDENT MOBILITIES OF NH_4^+ and Br^- IONS IN N_2 and O_2[a]

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The zero-field mobilities of Br^- and NH_4^+ in gaseous oxygen and nitrogen have been measured as a function of temperature. Our measurements were performed in a high pressure drift tube mass spectrometer which has been described previously.[1,2] The ions were produced by ^{63}Ni beta bombardment of the gases CF_3Br and NH_3 which were leaked into the source region. The ions were essentially in thermodynamic equilibrium with the drift gas in all of the measurements, since E/N (electric field strength divided by gas number density) was maintained below 6 Td (1 Td = 10^{-17} V cm^2).

The data are presented in Figures 1 and 2 in the form of a reduced mobility

$$K_o = (v_d/E)\ (P/760)(273.2/T)$$

where P is the gas pressure in Torr, T is the temperature in K, v_d is the drift velocity and E is the electric field strength.

In the Br^- measurements, the concentration of the gas CF_3Br was very small compared to the total carrier gas in the drift tube. The measurements were performed at drift gas pressures of 30-40 Torr for the higher temperatures, and 700-800 Torr for the lower temperatures. At several temperatures, the drift velocity was measured at both 30-40 and 700-800 Torr and the reduced mobility was observed to be the same to within 1%. The only major ion present in the negative spectrum in both oxygen and nitrogen was the Br^- ion itself. In the Br^- in nitrogen measurements at higher pressures, a very small amount of the first nitrogen cluster of Br^- was observed. However, mobility measurements were also performed at

lower pressures where no clustering was observed and the values were found to be equal.

In the NH_4^+ measurements, only a trace amount of NH_3 vapor was required for formation of the ions. The mobility measurements of NH_4^+ in nitrogen were performed with drift gas pressures of 700-800 Torr, while those of NH_4^+ in oxygen were performed at 30-50 Torr. In the NH_4^+ in nitrogen measurements at higher pressure, a small amount of the first nitrogen cluster of NH_4^+ was observed. The arrival time of this cluster was measured and a reduced mobility was calculated. It was found to be the same as the mobility of NH_4^+ at this same pressure. The value was then compared with the reduced mobility of NH_4^+ measured at 25-30 Torr where no clustering was observed and the values were again found to be equal. This observation, coupled with the fact that the symmetry of the NH_4^+ mobility peaks indicated no NH_4^+ reactions within the drift tube, led us to believe that the presence of the $NH_4^+ \cdot (N_2)$ ion was the result of nitrogen clustering in the aperture which separates the high vacuum mass spectrometer region from the drift tube. In both sets of NH_4^+ measurements, a small percentage of clustering reactions with NH_3 was observed at the lowest temperature.

The error in the K_o values for NH_4^+ and Br^- ions in nitrogen is believed to be $\pm$ 3% over the entire temperature range. The uncertainty at lower temperatures for the NH_4^+ measurements is primarily attributed to the influence of clustering reactions with NH_3. For Br^-, much of the lower temperature uncertainty arose from a larger than usual scatter in arrival time measurements. At higher temperatures, the uncertainty for both ions is attributed to possible non-uniformities in the drift gas temperature which become more pronounced at elevated temperatures. Improvements were

made in temperature monitoring of the drift gas, and the error in the K_o measurements in oxygen is believed to be $\pm$ 2% over the entire temperature range. An additional source of error for all measurements was pressure instability of the drift gas. Our value of K_o for Br^- in nitrogen at 415K is within 3% of the zero-field value given by Griffin, et al.[3] at 413K. To the best of our knowledge, none of the other ion mobilities has been previously measured and no calculation exists to which they can be compared.

a) Research supported by the Atmospheric Sciences Division of the National Science Foundation through Research Grant No. ATM-8016881.

b) School of Physics, Georgia Institute of Technology.

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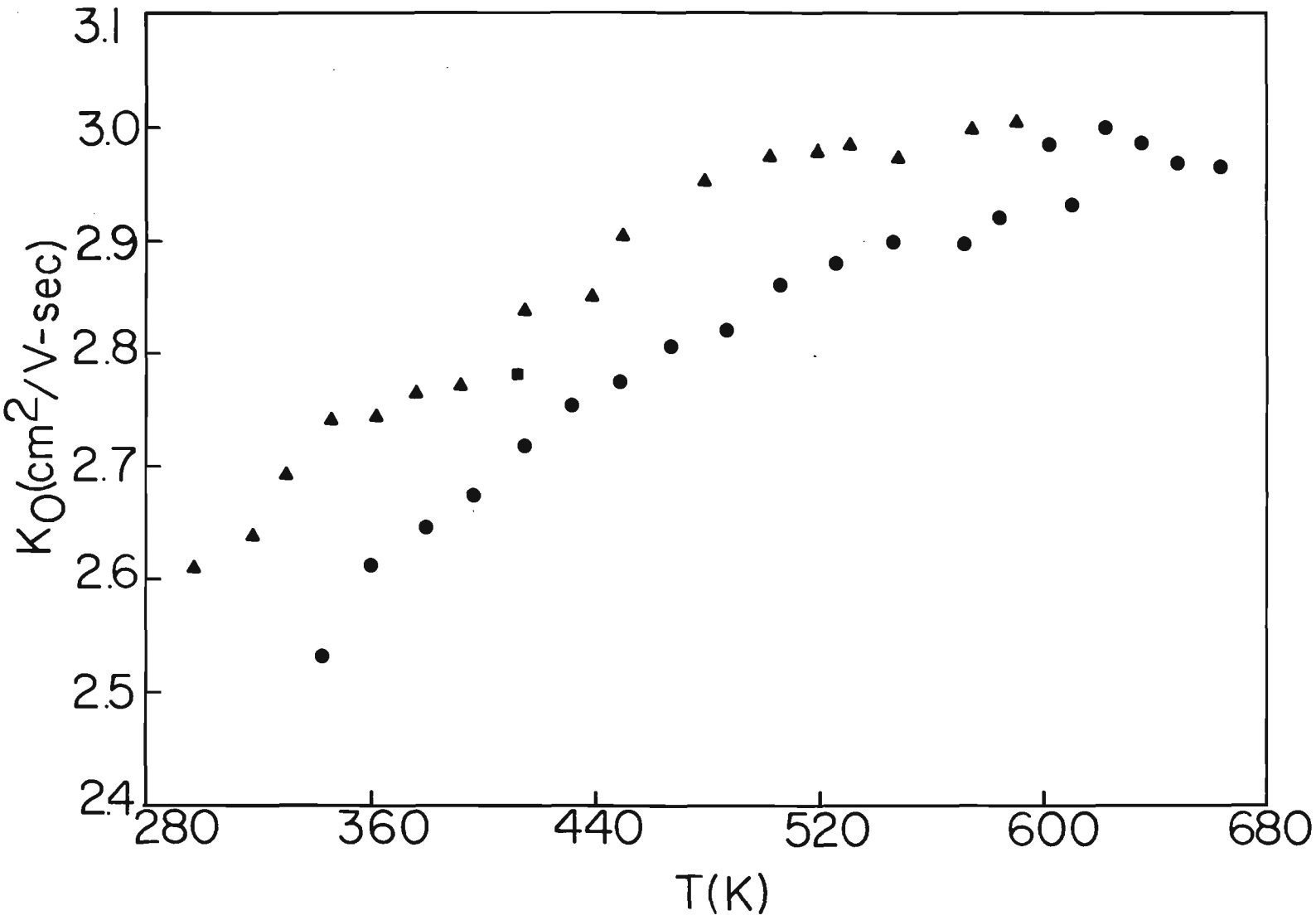

Figure 1.

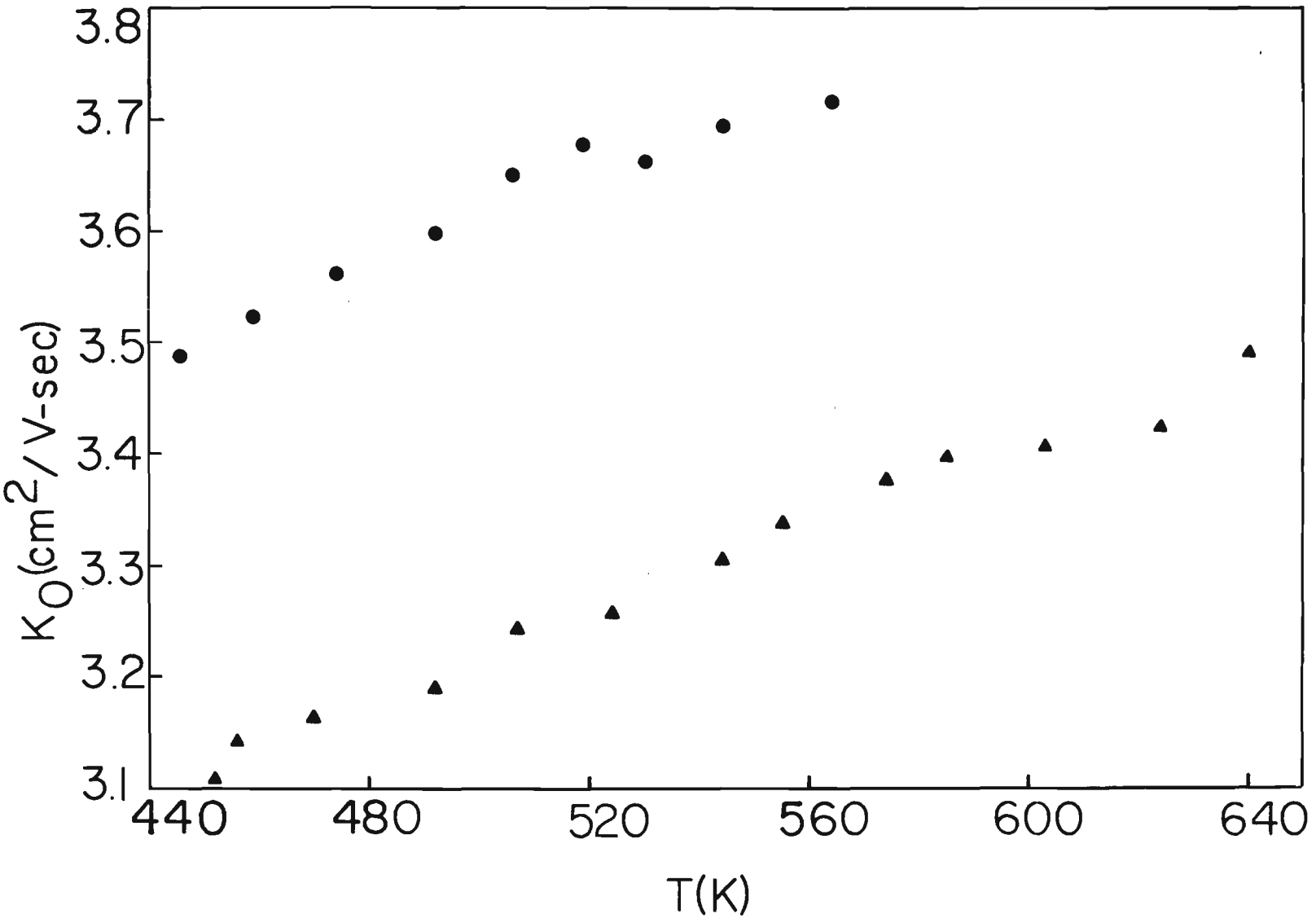

Figure 2.

Figure 1. The Reduced Mobility of Br^- in Oxygen, ▲ ; and in Nitrogen, ● as a Function of Temperature. The Reduced Mobility for Br^- in Nitrogen, ■ from Ref. 3.

Figure 2. The Reduced Mobility of NH_4^+ in Oxygen, ● ; and in Nitrogen, ▲ as a Function of Temperature.

Measurement of the mobilities of Cl^-, $NO_2^-\cdot H_2O$, $NO_3^-\cdot H_2O$, $CO_3^-\cdot H_2O$, and $CO_4^-\cdot H_2O$ in N_2 as a function of temperature[a)]

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The zero-field mobilities of Cl^-, and the first water clusters of NO_2^-, NO_3^-, CO_3^-, and CO_4^- in N_2 have recently been measured as a function of temperature in a high-pressure drift tube mass spectrometer.[1-3] Many of the measurements of Cl^- in N_2 were performed at a pressure of 740–780 Torr, while a few of the Cl^- and all of

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the water clustered ion mobilities were measured in 20–35 Torr of N_2. This lower pressure regime, in which $NO_2^- \cdot H_2O$, $NO_3^- \cdot H_2O$, $CO_3^- \cdot H_2O$, and $CO_4^- \cdot H_2O$ were studied, was required in order to allow the observation of the formation of these ion clusters from their parent ions. The ion cluster formation and/or breakup step resulted in a skewing of both the parent and clustered ion arrival time spectra which allowed us to determine the approximate ion cluster formation and dissociation rates.[4,5] We can then choose conditions such that the ions of interest undergo very few reactions before being destroyed. In addition, the skewed arrival time spectra help us to distinguish between reactions occurring in the drift region and those, if any, occurring at the exit aperture of the drift tube. There were no observed reactions involving Cl^- in the temperature range studied, so it could be studied at either high or low pressures. In fact, Cl^- measurements were made both at atmospheric pressure and at 20–30 Torr, and they resulted in the same value for reduced mobility. All measurements were made under approximately zero-field conditions with $E/N \leq 5$ Td (1 Td = 10^{-17} V cm^2), where E is the electric field strength and N is the gas number density.

Unlike most previous ion mobility measurements performed in this laboratory, the present study includes ions which were undergoing reactions in the drift region of our drift tube.

We have attempted to minimize the effects of these reactions by adjusting the water concentrations so that the ions of interest were at least several times more abundant than any other member of the ion cluster family. The total pressure and water concentration were adjusted to minimize the time available for additional reactions to occur once the first water cluster was formed from the parent ion. Finally, mobility values were calculated from the unskewed or only slightly skewed slope of an arrival time spectra which includes very few contributions from ions involved in reactions. While the diffusion coefficient must be included in this calculation, the uncertainty in the diffusion coefficient introduces little error since diffusion is quite slow at these high pressures. Despite these efforts, the uncertainties in our mobility measurements for the clustered ions are still quite high (as shown in Table I) with most of the uncertainty arising from reactions in the drift region and only about 1% uncertainty due to either pressure or temperature. The uncertainty quoted for Cl^- is nearly entirely due to possible errors in the temperature measurement since 760 Torr can be measured quite accurately and no reactions were observed. The larger uncertainty in temperature quoted for Cl^- compared to the water clustered ions reflects the much larger temperature difference between the drift tube and its surroundings, and the problems of measuring and maintaining temperature uniformity with a much larger temperature differential.

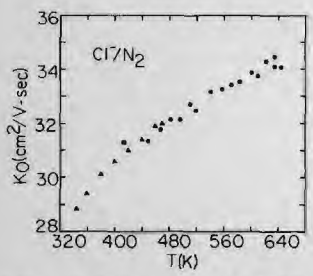

FIG. 1. The reduced mobility of Cl^- in N_2 as a function of temperature. Present measurements: ●; past measurements from our laboratory: ▲; data reported by Ref. 6: ■.

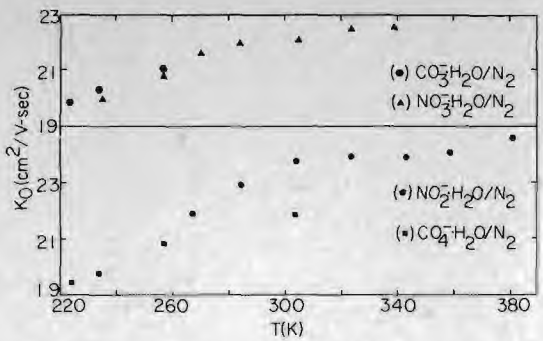

FIG. 2. The reduced mobility of $NO_2^- \cdot H_2O$: ●; $NO_3^- \cdot H_2O$: ▲; $CO_3^- \cdot H_2O$: ●; and $CO_4^- \cdot H_2O$: ■ in N_2 as a function of temperature.

Figure 1 shows the zero-field reduced mobility (K_0) of Cl^- in N_2:

$$K_0 = (V_d/E)(P/760)(273.2/T) ,$$

where P is the gas pressure in Torr, T is the temperature in K, V_d is the drift velocity, and E is the electric field strength. Also shown in Fig. 1 are values previously reported by our laboratory which cover a lower temperature range,[1] and a single fixed temperature measurement at 413 K (reported by Griffin *et al.*[6]). To the best of our knowledge there are no measurements covering the present temperature range, but agreement with the lower temperature measurements shown is quite good. Figure 2 shows the values of K_0 measured for $NO_2^- \cdot H_2O$, $NO_3^- \cdot H_2O$, $CO_3^- \cdot H_2O$, and $CO_4^- \cdot H_2O$, and Table I shows the uncertainties for all of the present mobility measurements. To the best of our knowledge, none of these mobilities have been measured previously and there are no calculations to which they can be compared. The measured mobilities of these water clustered ions, however, appear to have a temperature dependence quite similar to that of their parent ions.[3]

TABLE I. Uncertainty in the measured reduced mobility values. The range of uncertainty listed for Cl^- corresponds to low- and high-temperature measurements, respectively.

Ion	Uncertainty
Cl^-	±2%–±3%
$NO_2^- \cdot H_2O$	±4%
$NO_3^- \cdot H_2O$	±4%
$CO_3^- \cdot H_2O$	±4%
$CO_4^- \cdot H_2O$	+4%, −8%

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